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ON THE FRAGMENTATION OF FURAN MOLECULE AND ITS DEPENDENCE ON THE LASER WAVELENGTH

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1. INTRODUCTION

The fragmentation processes of the aromatic conjugated diene systems have been studied by many research groups [1–10]. Derrick *et al.* [1], have studied the electronic structure using photoelectron spectroscopy, where a number of highly excited Rydberg states were accessed, also they attributed the fragmentation of the furan molecule to the photoelectron energy responsible for the breaking of the C–C bond or the C–O bond. Rockwood *et al.* [10], using a fixed frequency KrF laser (249 nm), and Zandee and Bernstein [4], using nitrogen laser pumped dye laser, both found extensive ion fragmentation as the laser power density was increased. Cooper *et al.* [5] studied the fragmentation process of the benzene, pyrrole, and furan molecules using the resonantly enhanced multiphoton ionization technique; they stated that the fragmentation process for benzene was efficient at the highest laser power density $5 \times 10^9 \text{ W/cm}^2$, for furan molecule at a laser wavelength of 376 nm, in a two-photon resonance the parent ion was seen as the strongest peak, while at 550.5 nm in a three-photon resonance the parent ion was not seen in full laser power, and only appeared slightly at 54% of the laser power. Boesl *et al.* [6], in a work done on the fragmentation of furan, reported a weak dependence of the ion efficiency on wavelength.

Here in this study, the fragmentation of the furan molecule was examined, using jet-cooling, resonance enhanced multiphoton ionization REMPI, combined with TOF mass spectrometry.

Multiphoton mass spectrometry relies on lasers to tune to a resonant state as an intermediate step on the way to ionization with a further photon. This is essential as it is not only assures selectivity of the ionization events but also greatly reduces the intensity required for ionization. If the laser wavelength is not resonant with an absorbing molecular intermediate state, absorption of laser wavelength can still occur via virtual states, but at much higher levels of intensities. At high enough laser intensities, everything ionizes, even the background gas in the ion source. Once this non-discriminate excitation reaches ionization, extreme fragmentation usually results [11].

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2. EXPERIMENTAL

The laser radiation with an optimum energy of 30 mJ/pulse, was provided by a Lambda-Physik FL 3002 dye laser pumped by a Lambda-Physik EMG 201 MSC excimer laser. The laser beam was focused with a 6-cm-focal length lens into a molecular beam of furan in He. The beam was generated by pulsing ~ 760 torr of 5 % furan in He through a nozzle (General Valve, aperture 250 μm) into the ionization chamber of the time-of-flight mass spectrometer (TOF-MS), where the pressure is kept below 10^{-6} Torr. The ion signal from the TOF-MS was processed by Stanford Research SR 250 boxcar integrator and stored on a PC.

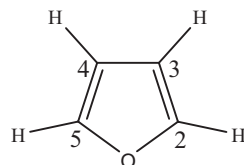


Figure 1. The molecular structure of furan molecule showing the $C_2 - C_3$, $C_3 - C_4$, $C_4 - C_5$ bonds

3. RESULTS

Figure 2 shows the mass spectra of furan at different laser wavelengths. It is obvious from the spectra that the fragmentation process differed according to the laser wavelength. The molecular ion $C_4H_4O^+$ is apparent, and has the highest peak between 334 – 363 nm laser wavelengths. But, at a laser wavelength of 327 nm, the fragment ion $C_3H_3^+$ appears to have the highest peak followed by the molecular ion $C_4H_4O^+$. At a laser wavelength of 321 nm, the molecular ion $C_4H_4O^+$ diminishes, and is only seen very weakly, the fragment ion C^+ appears to have the second highest peak after the $C_3H_3^+$ peak. So far it appears that as the laser wavelength is moved to higher energy (shorter wavelengths), the molecular ion $C_4H_4O^+$ undergoes fragmentation, first into the parent ion $C_3H_3^+$, then into CHO^+ , C_2^+ , and C^+ fragment ions. Finally, when the laser wavelength reaches 308 nm, the molecular ion $C_4H_4O^+$ completely disappears, and the highest peak is that of the C^+ fragmentation.

4. DISCUSSION

From the mass spectra in Figure 2, it can be deduced that the molecular ion $C_4H_4O^+$ undergoes fragmentation as the laser wavelength is moved to shorter wavelengths (higher energy). Laser power density had little effect on the fragmentation process, with an approximate power density of 1×10^{10} W/cm² for the fundamental dye laser wavelength between 327–363 nm. For the frequency doubled output between 308–321 nm, the power density dropped to approximately 1×10^9 W/cm². In both cases the power density is considered too high. In fact the fragmentation process should be reversed as the laser power is dropped, but instead we see the opposite. Therefore, another reason for the fragmentation must be introduced. First consideration is the resonance of the laser wavelength with the intermediate state. Almost all laser wavelengths 363 nm, 334 nm, 327 nm, 321 nm, and 308 nm, are resonant at two-photon energy level with either valence intermediate states or Rydberg states. But at a four-photon energy level, the laser wavelengths 363 nm, 334 nm, and 327 nm are resonant with higher excited ionic states, whereas the 321 nm and 308 nm are not. The most convincing consideration is to assume the energy required at the three-photon energy level to break the C – C bond or the C – O bond. In furan, according to Derrick *et al.* [1], the $1a_2$ orbital (Π_1 or Π_3) attributed to the $C_2 - C_3$ or the $C_4 - C_5$ bonds has an IP of ~ 71180 cm⁻¹ (8.9 eV), the $2b_1$ orbital (Π_2) attributed to the $C_3 - C_4$ bond has an IP of 83074 cm⁻¹ (10.3 eV), and the $1b_1$ orbital attributed to all the $C_2 - C_3$, $C_3 - C_4$, $C_4 - C_5$, and C – O bonds has an IP of ~ 116143 cm⁻¹ (14.4 eV), whereas the $9a_1$ orbital of the strong $C_2 - C_3$, $C_3 - C_4$, and $C_4 - C_5$ bonds has an IP of ~ 104851 cm⁻¹ (13.0 eV), see Figure 1.

The dominant peak in the mass spectrum (a) in Figure 2 is that of the $C_4H_4O^+$ molecular ion, with smaller peak for the fragment ions C^+ , CHO^+ , C_2^+ , and $C_3H_3^+$. This fragmentation process correspond to an energy region of $82\,644$ cm⁻¹ (10.25 eV) at the three-photon level, or $110\,192$ cm⁻¹ (13.66 eV) at the four-photon level, with a fundamental dye laser power density of $\sim 1 \times 10^{10}$ W/cm². As it can be seen, the laser power has almost no effect on the extent of fragmentation. It is obvious though, that at the four-photon level the energy would have exceeded the IP for the $1a_2$, $2b_1$, and $9a_1$ orbitals. Hence, the formation of the fragment ions can be explained, since only the C – C bonding is breakable in this case. The mass spectrum (b) in Figure 2, still shows the molecular ion $C_4H_4O^+$ as the dominant peak, followed by the $C_3H_3^+$ fragment ion; here in this case at the four-photon level, the energy region will correspond to $119\,760$ cm⁻¹ (14.85 eV), this exceeds the IP for the $1b_1$ orbital, attributed to all C – C bonding and C – O bonding, and also exceeds the IP for the $6b_2$ orbital attributed to the strong C – H bonding. Although the $C_4H_4O^+$ molecular ion has the strongest peak, the formation of the $C_3H_3^+$ fragment ion is an indication of the breakage of the C – O bond and C – H bond. The mass spectrum (c) in Figure 2, corresponds to an energy region of $122\,324$ cm⁻¹ (15.17 eV) at the four-photon energy level;

here the dominant peak is that of the fragment ion $C_3H_3^+$ followed by the molecular $C_4H_4O^+$ ion, this energy region exceeds the IP for the $8a_1$ orbital attributed to the strong C – H bond. The molecular $C_4H_4O^+$ ion is starting to fragment at this high energy region. The molecular $C_4H_4O^+$ ion almost disappeared in the mass spectrum (d) in Figure 2, only a small trace is visible. While the $C_3H_3^+$ and C^+ fragment ions show strong and equal intensities, this energy region corresponds to 124610 cm^{-1} (15.45 eV) at four-photon level, which exceeds the IP's for all the orbitals mentioned previously. This explains the extent the fragmentation process for the molecular $C_4H_4O^+$ ion underwent. The final mass spectrum (e) in Figure 2, shows that the $C_4H_4O^+$ molecular ion has completely vanished, indicating complete fragmentation. This can be explained from the appearance of the C^+ fragment ion as the dominant peak, then followed by the C_2^+ fragment ion, then the $C_3H_3^+$ and CHO^+ fragment ions, here the energy region corresponds to 129870 cm^{-1} (16.1 eV). This exceeds the IP's for all the orbitals mentioned so far, in addition to the $5b_2$ orbital attributed to the C – O bond. Hence, we see complete fragmentation process at a laser wavelength of 308 nm, provided by the frequency doubled output of the dye laser.

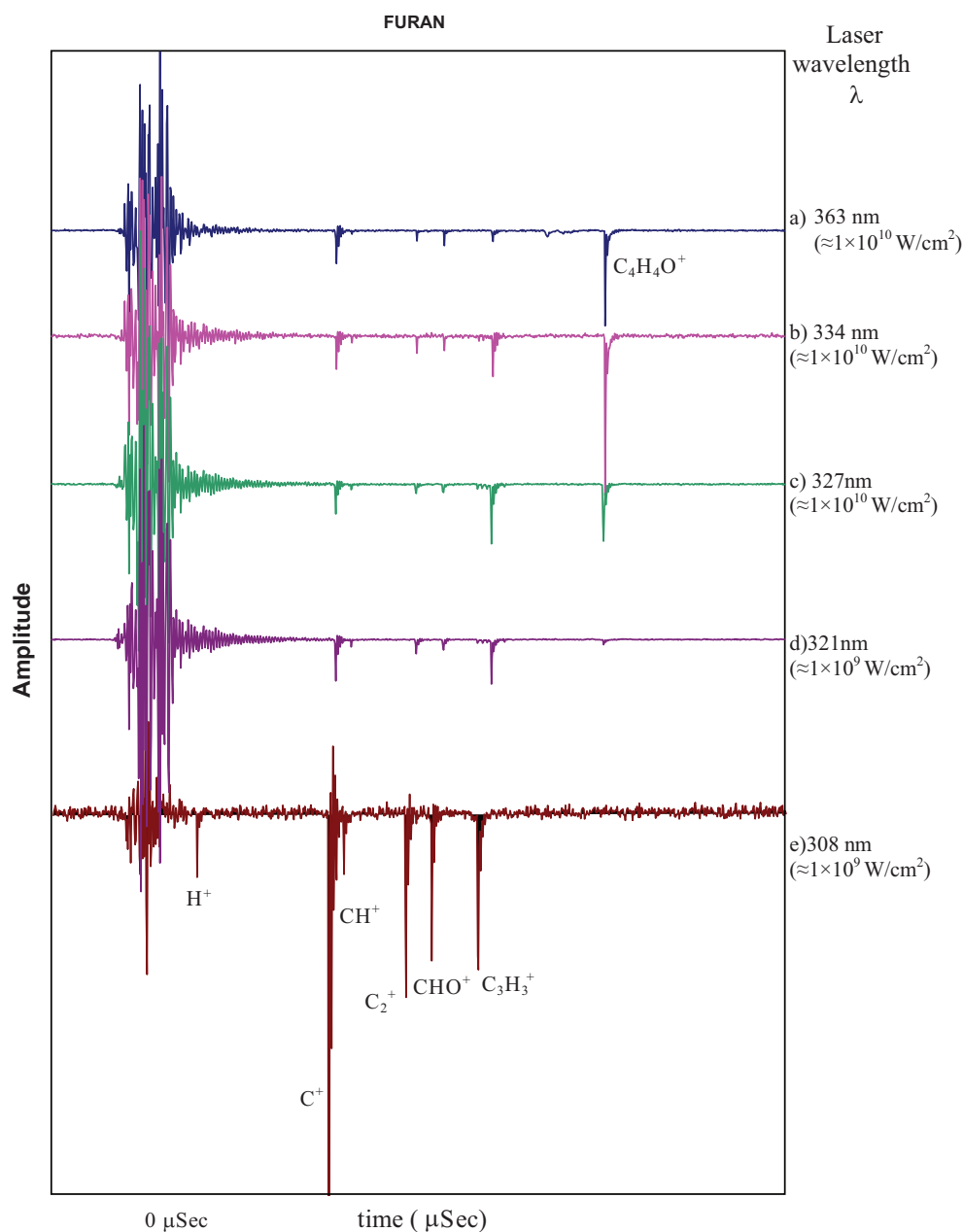
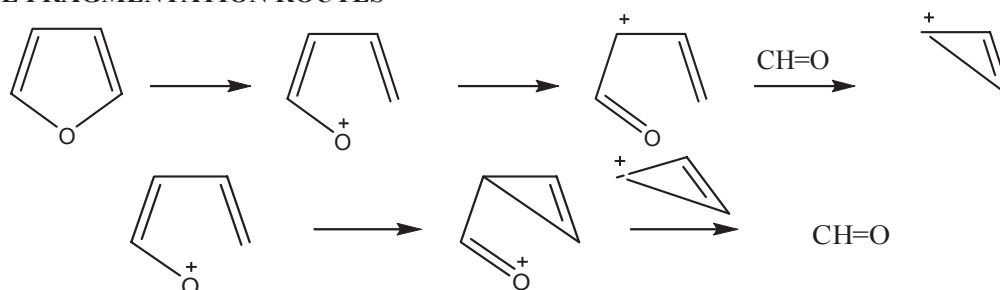


Figure 2. Excitations at different laser wavelengths, showing the fragmentation process of the furan molecule at those laser wavelength

5. POSSIBLE FRAGMENTATION ROUTES



6. CONCLUSION

The unfavorable assumptions that the absorption cross-section to a four-photon level would be reduced as a consequence of absorbing four photons coherently, can be matched by the high laser power density of $\sim 1 \times 10^9$ W/cm². One most important factor is the presence of resonant states at the two-photon energy level for all the mass spectra in (a), (b), (c), (d), and (e), whereas at the four-photon energy level only the spectra in (a), (b), and (c) are resonant with highly excited ionic states, the mass spectra in (d) and (e) are only slightly resonant. The disappearance of the parent C₄H₄O⁺ molecular ion in the spectra (d) and (e), is at the four-photon energy, will have reached the IP's of the C – O and C – H bonds, hence complete fragmentation.

The presence of intermediate states at the two-photon energy level enhances the coherent excitation, and the absorption cross-section would be large enough for absorbing more photons to higher excited states. There are no intermediate states at the three-photon energy level. Hence, more photons need to be absorbed to reach resonant states at the four-photon energy level, a factor that is met by the high laser power density of $\sim 1 \times 10^9$ W/cm². Therefore, two factors determined the extent of fragmentation for the furan molecule, as the laser wavelength moved to higher energy (shorter wavelength). First, the laser wavelength must reach or exceed the IP of the orbitals attributed to the C – C, C – O, and C – H bonds. Second, there should be resonant intermediate states for an enhanced absorption and therefore efficient ionization.

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